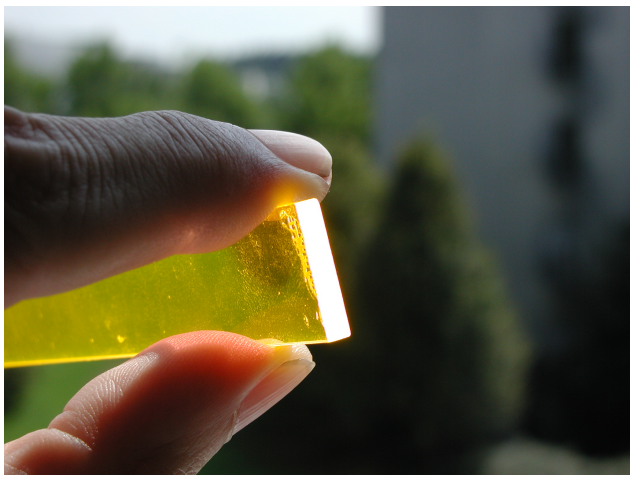
Habilitationsschrift

PRIMARY METHODS OF GENERATING SOLAR POWER BY USING THE TARGETED MODIFICATION OF FLUORESCENT SYSTEMS

Translated to English from

PRINZIPIELLE WEGE FÜR DIE GEWINNUNG VON SOLARENERGIE ÜBER GEZIELTE MODIFIZIERUNG FLUORESZIERENDER SYSTEME



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PRIMARY METHODS OF GENERATING SOLAR POWER BY USING THE TARGETED MODIFICATION OF FLUORESCENT SYSTEMS

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Energy is needed in all areas of technology, and more and more new ways to obtain primary energy are being sought. In particular, energy sources that cannot be exhausted and can ensure a supply of energy over long periods of time are of interest. Solar energy is a nearly unlimited primary energy source that is so far only directly being used to a minor extent. This lack of use is because solar power (and thus solar energy), although present in large quantities, is distributed over large areas, in contrast to other primary energy sources (the AM1 spectrum[1)] delivers at the full incidence of light,[2)] approximately 800 $W \cdot m^{-2}$). As a consequence, the recovery of solar energy requires completely new technologies.

The low power density of solar energy precludes an economic use for purely thermal operations, as technically achievable temperatures are too low for most applications. Furthermore, energy converter systems, such as photovoltaic cells, are relatively expensive and must be installed over a large area.

The economically feasible operation of solar systems therefore requires concentrators for solar power density that are upstream to the actual utility or conversion system.[3)] So far, mirrors and, to a lesser extent, lenses have been used to obtain light concentration via geometric optics. However, geometric optics[4)] can only focus direct radiation, but not diffuse radiation, for thermodynamic reasons.[5)] Concentrators with geometric optics are therefore best suited for desert regions with predominantly direct solar radiation. Plants of this kind are hardly economical to operate in more temperate latitudes, where a large part of the solar radiation is diffuse.

One possible way to concentrate even diffuse sunlight is by using the fluorescence solar collector developed by Garvin,[6)] Goetzberger and Greubel.[4)] This collector consists of a plane-parallel plate made of transparent, highly refractive material, e.g., PMMA (*Plexiglas*), with $n_D^{20} \approx 1.5$ that is homogeneously colored with a fluorescent dye (Figure 1). Light radiation *I* from all directions hitting the surface of the plate penetrates into the optically denser material (with refraction of light) and is absorbed by the homogeneously dissolved dye. The fluorescent light F_1 ... F_4 then becomes (statistically) almost isotropically scattered in all spatial directions.

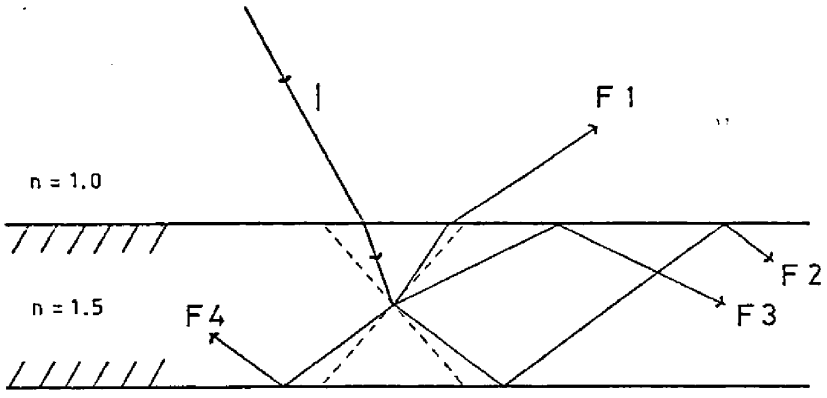


Figure 1. Operation of the fluorescence solar collector. *I*: Incident light beam, F_1 ... F_4: Fluorescent light.

Of the emitted fluorescent light, however, only a small part, F_1, directly leaves the plate again, which hits the plate surface at an angle steeper than that of the critical angle of total reflection.

Most of the fluorescent light (F_2 ... F_4) is guided by total reflection in the plate and leaves only at the edge surface again. Because the area of the plate is much larger than the edge surface, the light is concentrated, which, in practice, can reach a factor of 200.[4)] The maximum achievable concentration is exp ($h\Delta\nu/k_BT$), where $\Delta\nu$ is the Stokes' shift of the specific fluorescence dye used.[5)]

Problem outline

The construction of fluorescence solar collectors involves the use of fluorescent dyes and dye-matrix-combinations, combining distinct properties not found in any known substance class or substance combination. Basic and principal solutions should be developed to form the basis for other selectively absorbing solar systems. The results are not limited to fluorescence solar collectors but also allow insights into other areas of chemistry.

The most important properties required by fluorescent dyes can be summarized by the following topics:[7)]

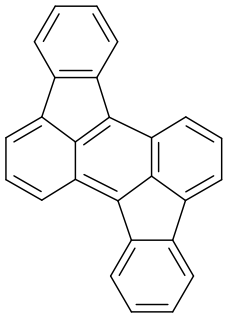
1. Homogenous solubility in an organic matrix;
2. Very high lightfastness (photostability);
3. Fluorescence quantum yields of nearly 100%;
4. Various dyes with absorptions in all regions of the visible to near IR radiation;
5. Low overlap between absorption and fluorescence spectra.

Subproblems 1 - 5 are individually treated below.

1. Solubility

The solubility of aromatic systems in organic solvents is known to decrease with the increase in the number of linked ring systems,[8)] and with a sufficient number of rings, such systems are completely insoluble in common organic solvents at room temperature. However, aromatic polycyclic systems are required as chromophores for light absorption in the long-wavelength visible or near IR range. In the dyeing technique, such dyes are applied in most cases as pigments[9,10)] (e.g., indanthrene dyes in textile dyeing), in which low solubility is a desirable side effect. In the fluorescence collector, however, particles form scattering centers and lower the efficiency of the system. Therefore, in this application, all dyes must be distributed homogeneously.

Research on fluorescent dyes for solar collectors showed[11)] that substituting with *tert*-butyl groups generally increased the solubility of aromatic systems in organic solvents significantly (see also ref.[12)]). This principle has been successfully applied to dyes of very different structures, e.g., to rubicene (**1**) derivatives[11,13)] (RN 197-61-5) or perylene dyes **2**[11,14)] (see further below). The replacement of a hydrogen atom by a *tert*-butyl group increases the solubility by a factor of approximately 10. This is true for alcohols (methanol), aromatic solvents (toluene) and aliphatic hydrocarbons (*n*-hexane) and has been studied extensively on rubicene derivatives using the UV/VIS absorption of saturated solutions.[13)]



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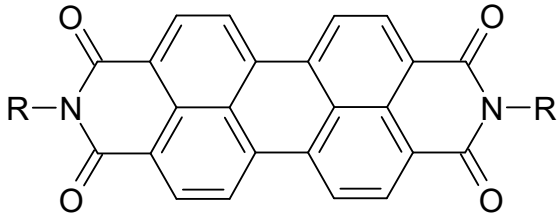
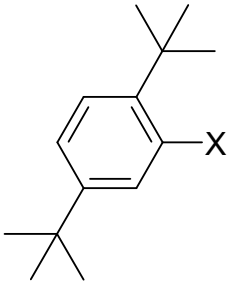
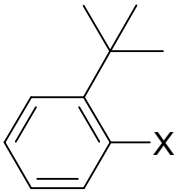
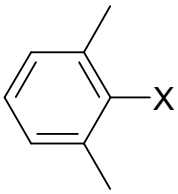


2

The stem compound **1** is only very slightly soluble in alcohols and alkanes and sparingly soluble in aromatic solvents such as toluene. The solubility successively increases by introducing 1, 2 and 4 *tert*-butyl groups (the substitution of the 5 and 13-positions of di-*tert*-butylrubicene **1a**, RN 78915-10-3, as proven by X-ray analysis[15]), and the increase in solubility reaches a factor of approximately 10^4 in toluene for tetra-*tert*-butylrubicene. Measurements of the solution enthalpy indicated that the introduction of the first *tert*-butyl group contributes more to the increase in solubility than that of the following groups.[13] The introduction of *tert*-butyl groups is particularly advantageous, as the photostability of dyes is generally not adversely affected, as shown in perylene dyes **2** (see Table 1).

Table 1. Examples of perylene dyes **2**.[a]

Substituent R in **2**[b]	Quantum yield[c]	Photostability[d]	CAS RN
	1:00	1.9	83054-80-2
	0.94	2.9	80509-63-3
	0.98	≡ 1	76372-76-4

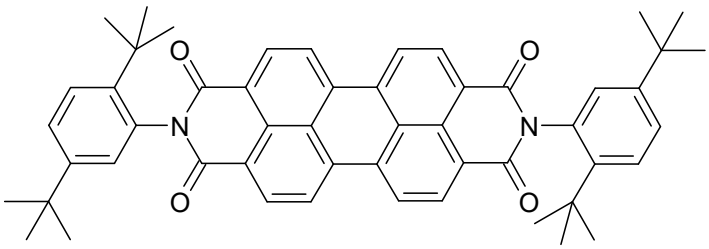
a) For further examples see refs.[14,16]. - b) Substituents R in **2**. -
c) Quantum efficiency in DMF. - d) Relative photostabilities; see also ref.[14,16]

It is also beneficial that the introduction of these groups hardly changes the absorption and fluorescence spectra, and the fluorescence quantum yields usually even (slightly) increase (see Table 1). These substituents can be often easily introduced by electrophilic or nucleophilic substitution of the dyes themselves or of their precursors.[16]

2. Photostability

A minimum lifespan of 5 - 20 years for solar collectors should be realized in order to be economical. Taking simplistic assumptions and consideration for the special properties of the

fluorescence collector system, a quantitative relationship between the quantum yields of the photobleaching reactions of the applied dyes and the lifetime of the system can be established.[17] The quantum yields for the photo bleaching reactions must not exceed 10^{-8} to 10^{-9} (see Figure 2). In addition, photolysis products must not quench the fluorescence. Dye systems that meet these conditions were realized by the combination of very photostable chromophores with very photostable auxochromic groups.[14] This served as the basis for the development of stable vat dyes. For example, it is known that the perylene skeleton is particularly suitable for photostable dyes. On this basis, perylene dyes **2** have been synthesized,[14] which fairly reasonably meet the requirements for fluorescence collectors. A phenyl ring substituted with *tert*-butyl groups[11,14] was preferred for R in order to have a sufficiently high solubility (see also Table 1). A dye with the substitution shown in **3** proved to be a convenient compromise between quantum yield, photostability and solubility.



3

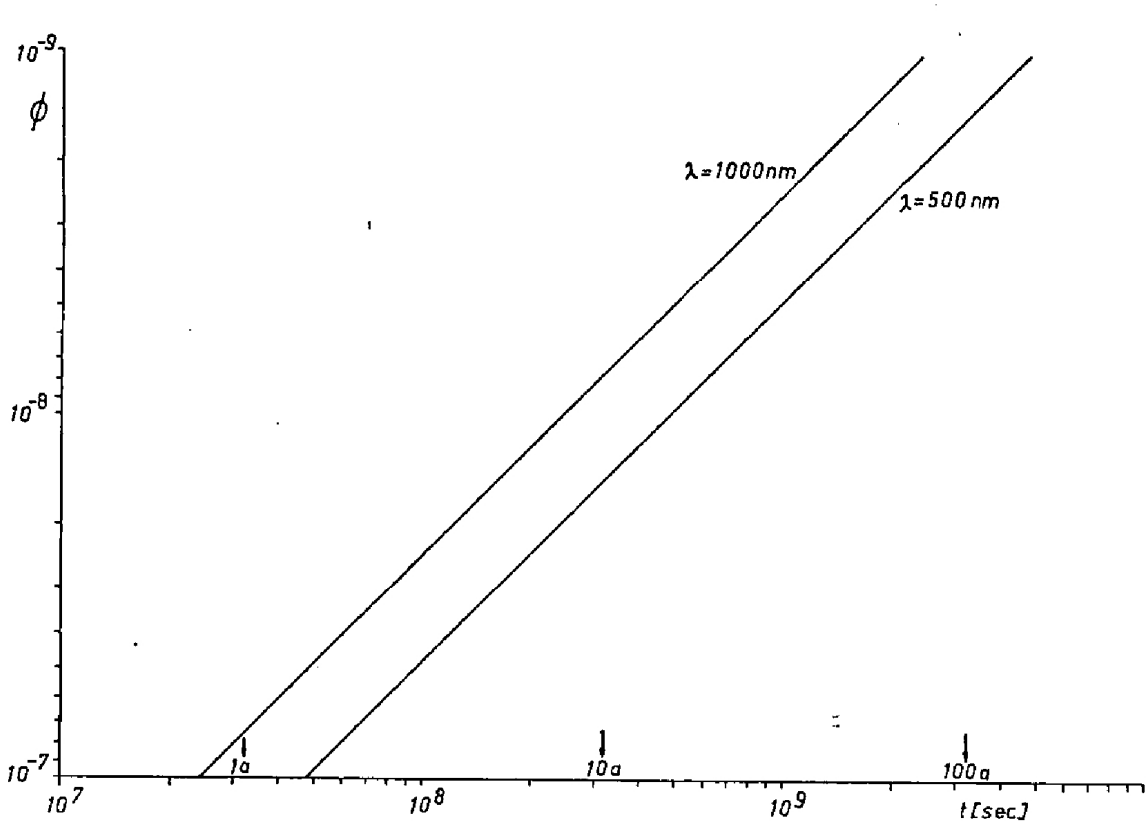


Figure 2. Relationship between the lifetime of solar collectors and the quantum yields of the photobleaching reactions of the applied dyes. The straight lines refer to the average absorption wavelengths of 500 and 1000 nm.

Singlet oxygen seems to play a key role in photobleaching reactions because it can destroy the chromophore in certain cases by Diels-Alder analogue or En reactions. Singlet oxygen is formed by sensitization by the dye itself via the T_1 state.[18] Singlet oxygen quenchers, such as 1,4-diazabicyclo[2.2.2]octane[19] (RN 280-57-9), may be applied to protect the dye from bleaching. This mechanism was examined in detail in the dye rubrene (RN 517-51-1). The results showed that there could be transfer to other dyes, e.g., benzo[*c*]cinnoline (RN 230-17-1). The photostability of the latter could be doubled in PMMA (Plexiglas) by the addition of 2.5% 1,4-diazabicyclo[2.2.2]octane. To optimize the protection against singlet oxygen, one might think of linking the quencher directly to the dyes.
To quickly test the photostability of extremely photostable dyes, an irradiation system was developed with which large-area samples can be exposed to visible light with more than 100 solar intensities. The photostabilities obtained with this arrangement can be correlated with values from long-term experiments under natural sunlight. Models of solar collectors made of PMMA (*Plexiglas*) were also practically tested. The collectors were treated with dyes by three different methods:

1. Mixing with PMMA (*Plexiglas*) granules and melting (processed by the company Röhm in cooperation with the IAF Freiburg);
2. Mixing with monomer and subsequent polymerization; and
3. Diffusion of the dye into the finished PMMA plates.

The latter method is advantageous because various dyes can be applied to the same type of finished PMMA support, and faded collectors can be reloaded.

3. Quantum yield

Little is known about the structure - fluorescence quantum yield relationship. Radiationless deactivation and intersystem crossing to the triplet state are the main processes competing with fluorescence.[20]
To avoid radiationless deactivation by predissociation,[20] dyes should not contain groups with weak bonds, such as nitro or methoxy groups. Further deactivation pathways that should be avoided result from the presence of conformationally labile groups or by groups that have a proton shift and consume the excitation energy. The dye should not contain heavy atoms such as bromine to keep the intersystem crossing low.
Furthermore, there should not be an overlap between electronic excitation and fluorescence ($\pi \rightarrow \pi^*$ excitation is generally favourable).
It has been found that the purity of the dyes is of particular importance since impurities from the synthesis can sometimes be very efficient fluorescence quenchers; an example of this is benzo[*c*]cinnoline. Considering these statements, dyes with fluorescence quantum yields of up to 100% have been obtained[14,16] (see also Table 1).

4. Absorption in the long-wavelength region in the visible to near IR range

For shorter wavelengths, dyes that meet some of these requirements have already been obtained. However, problems arise in the long-wavelength visible and IR regions. Efforts to obtain photostable dyes that fluoresce in the IR region with high quantum efficiencies have not been successful. Starting from vat dyes may be a promising route toward obtaining fluorescent dyes with corresponding properties.

5. Minimum overlap between absorption and fluorescence spectra

In a solar collector, fluorescent light is guided over longer distances for collection. In practical operation, one calculates a medium propagation between 1 and 5 m,[4] which even in a spectral range corresponding to relatively low dye extinction coefficients an almost complete absorption of light occurs, according to the Lambert-Beer Law. In particular, the short-wavelength components of the fluorescent light are captured by the long-wavelength spur of

the absorption spectrum. A reabsorption of the fluorescent light, however, leads to light losses;[4] therefore, the operation of fluorescence solar collectors requires dyes in which the absorption and fluorescence spectra are as separated as possible (minimum overlap). This central problem is examined in detail and is discussed below.

The Stokes shift is only a relatively coarse measure of the spectral separation of the dyes, since it does not consider the band shape. A mathematical model[21] has been developed for the quantitative description of the overlap, explicitly expressing the overlap integral of the spectra. It has been assumed that both the absorption and the fluorescence spectra can be composed as the sum of Gaussian functions, and this assumption is fulfilled with great accuracy for the longest wavelength subband of the absorption spectrum and the shortest wavelength band of the fluorescence spectrum (0-0 transitions). This assumption was confirmed by a precise analysis of the spectral edges of the dyes.[21] Under the stated conditions, a method has been developed to determine variances, e.g., for the 0-0-transitions, by using a purely graphical procedure that can describe the overlap integral S in a closed form, which is composed of an exponential and a pre-exponential factor.

The pre-exponential factor, which essentially contains an amplitude factor and the harmonic average of the σ^2 values for absorption and fluorescence, only linearly contributes to the numerical value of S. Its influence on S is relatively low. The exponential factor is a characteristic measure and the most important factor. The separation number, Tz, for the exponential factor is calculated by using Equation (1), where ST is the wavenumber difference between the 0-0-transitions in absorption and fluorescence.

$$Tz = e^{\frac{ST^2}{2(\sigma_A^2 - \sigma_F^2)}} \qquad (1)$$

σ_A and σ_F are the variances of these bands in absorption and fluorescence. Tz can be defined as a dimensionless number with a value ranging from 1 to $+\infty$ that grows with increasing separation (shrinking S). The Tz value should be more than 30 (150 is better) for the fluorescence collector. Thus, an important characteristic parameter is defined to estimate the usefulness of the dyes for solar collectors.

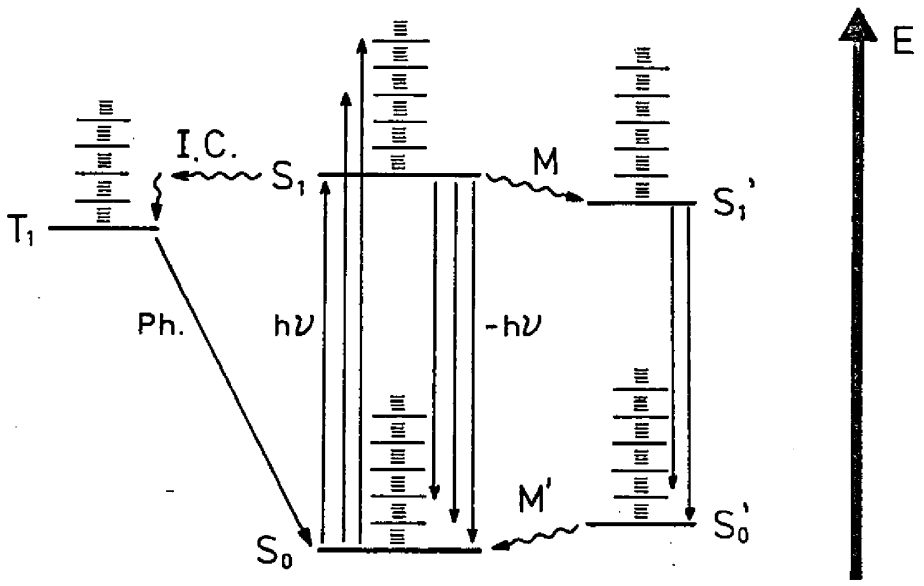


Figure 3. Jablonski diagram for absorption and fluorescence. M, M': Modification of the dye.

The possible mechanistic pathways for achieving a spectral separation between the absorption and fluorescence spectra are clearly depicted in the Jablonski diagram in Figure 3. Absorption is shown the as the transition between the S_o and S_1 states, and fluorescence occurs between the S_1 and S_o states.

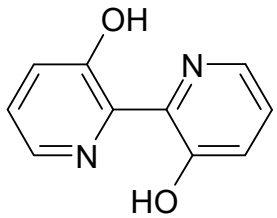
The transition at the longest absorption wavelength and the shortest fluorescence wavelength, the 0-0-transitions, are equal in energy, as seen in Figure 3. This results in the known phenomenon of spectral overlap between the absorption and fluorescence spectra and is a consequence of the properties described herein.[20)]
The excited state must be modified to reduce this spectral overlap (see M in Figure 3); this means that any reaction has to proceed by lowering its energy. The modified S_1' state can then descend via radiation to the modified ground state, S_o'. Since the dyes used in fluorescence collectors cannot be consumed, only processes come into consideration, where finally the ground state S_o is reached again as a cyclic process:

1. Excitation by absorption ($S_o \rightarrow S_1$),
2. Modification M for energy-lowering ($S_1 \rightarrow S_1'$),
3. Fluorescence ($S_1' \rightarrow S_o'$),
4. Modification M' to the ground state ($S_o' \rightarrow S_o$).

Processes within the scope of a certain time window are suitable for the modification M. The optical excitation S_o occurs in approximately 10^{-15} sec.[20)] The lifetime of the excited state S_1 is on the order of 10^{-9} to 10^{-7} sec. The modification must therefore not take longer than 10^{-15} sec but must be completed within 10^{-9} sec. This favorable time range corresponds approximately to the duration of one molecular vibration, i.e., the times of nuclear movements. Fast chemical reactions or fast relaxation mechanisms can therefore take place, e.g.:

1. Excimer formation,
2. Change of conformations,
3. Proton transfer reactions, and
4. Relaxation reactions of the solvent shell.

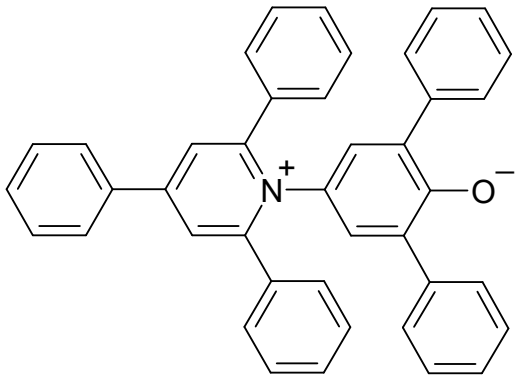
Of these, mechanisms 3 and 4 are the most promising for achieving large Stokes' shifts, and therefore were the subject of prior studies. An example of 3 is the Förster mechanism,[22)] which can be observed in fluorescent systems where OH or NH groups exhibit a much larger acidity in the excited state than in the ground state. Under certain conditions, light absorption by the protonated ground state S_o can be achieved, as well as fluorescence of the deprotonated S_1' state. A well-known example of a dye that exhibits fluorescence according to the Förster mechanism is hydroxypyrenetrisulfonate[22)] (RN 27928-00-3, RN 6358-69-6). Currently, bis-hydroxybipyridyls, in which the proton transfer can proceed intramolecularly, are being studied for their usefulness in fluorescent solar collectors.
The basic compound, dye **4** (RN 36145-03-6), was kindly provided by Prof. Witzel, University of Münster.



4

The loosening and forming of bonds, however, is disadvantageous because the color system is relatively heavily stressed, and side reactions that lead to its destruction can occur. For example, the low photostability of hydroxypyrenetrisulfonate is known.[23)] Thus, mechanism 4

is more favorable, which leaves the constitution of the dyes unchanged during the entire cycle. One can proceed with fluorescent dyes, in which the dipole moment changes in direction or size due to the optical excitation. The modification M in these cases is a relaxation of the solvent shell to adjust to the modified dipole upon excitation. After fluorescence, a relaxation (M') also must occur, as the dipole moment of the dye has now returned to its initial value.
The modification in polar media can be much more efficient than in less polar media. Therefore, a polar medium is needed for good spectral separation. As a consequence, mechanism 4 begs the fundamental question of how the polarity of a medium is defined and how it can be influenced.
The polarity of a medium, and especially of liquids, has been of interest for a long time.[24] Macroscopic physical quantities, such as the refractive index or the dielectric constant, represent only relatively rough measures of polarity[24] in the description of solvation. (For example, formamide with $\varepsilon = 110$ exhibits a significantly higher dielectric constant than water: $\varepsilon = 80$. However, as a medium in chemical reactions it is significantly less polar.)
Important progress was made with the establishment of empirical polarity scales, deriving a measure for polarity directly from a solvent-dependent process. Such scales include the Winstein *Y* scale,[25] which uses the rate constant for the solvolysis reaction of *tert*-butyl chloride as a polarity probe, and the $E_T(30)$ scale,[26] based on the strong solvatochromism of pyridinium phenolate **5** (RN 10081-39-7).



5

The $E_T(30)$ values are the molar excitation energies of the solvatochromic band of **5** in the solvent to be investigated and are calculated from the λ_{max} of this band by using Equation (2).

$$E_T(30) = 28590\ [\text{kcal} \cdot \text{mol}^{-1} \cdot \text{nm}] / \lambda_{max} \qquad (2)$$

The vast number of empirical polarity scales correlate linearly with each other, which is important for future investigations.[24,27,28] As a consequence, there must be a universal scale; however, so far only empirically determined measures of polarity for chemical problems exist, where the $E_T(30)$ scale representatively reflects polarity effects.
Since PMMA (polymethyl methacrylate, *Plexiglas*) is presently the most appropriate matrix for fluorescent dyes[4], it must be modified so that it provides as polar an environment as possible for the dissolved dye. However, this should not happen at the expense its favorable optical properties. The polarity increase can be achieved by a low molecular weight, polar additive, or by copolymerization with a more polar component. Such an addition should be very effective in small proportions in order to leave the properties of PMMA essentially unaffected. Tests for copolymerizations with methacrylic-2-hydroxyethyl ester (HEMA), for example, showed that although there was a significant increase in the polarity of the polymer

(e.g., improvement of the solubility of organic salts), the optical properties had considerably deteriorated (even in a relatively low polar fraction). Therefore, low molecular weight polar additives were introduced to attempt to increase the polarity, as it is now known that they can be incorporated into polymer matrices (e.g., plasticizers).
This problem leads to the question of how the polarity of a mixture changes with its composition. In particular, an equation with only few parameters that quantitatively describes this relationship would be highly useful. In the literature, plots of the polarity of binary mixtures (e.g., in the $E_T(30)$ scale[29]) against the composition of the mixture (e.g., in vol. % of the more polar component) in an overwhelming number of cases did not result in straight lines, as was initially expected;[29-31] instead, curved graphs have been obtained. (For a review of such works, see refs.[29,32]).

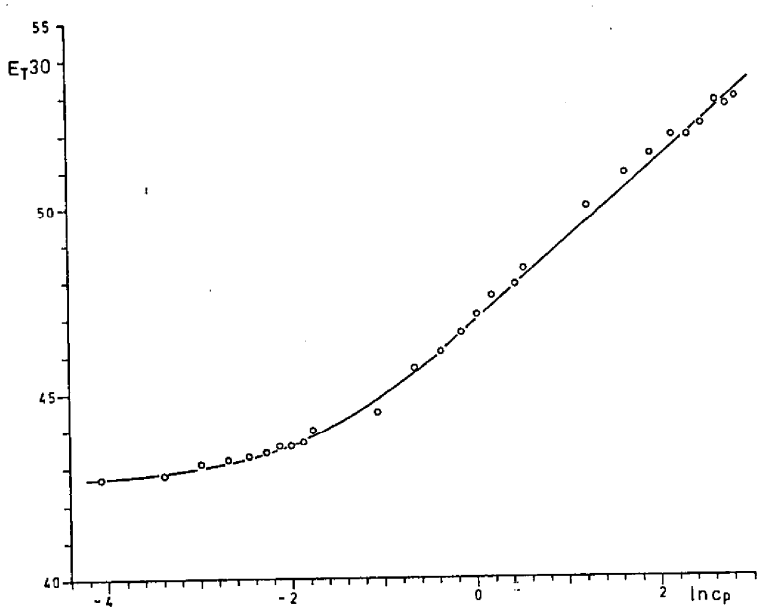


Figure 4. Relationship between $E_T(30)$ and ln c_p for a methanol/dioxane mixture; c_p: Concentration of methanol in mol · L^{-1}.

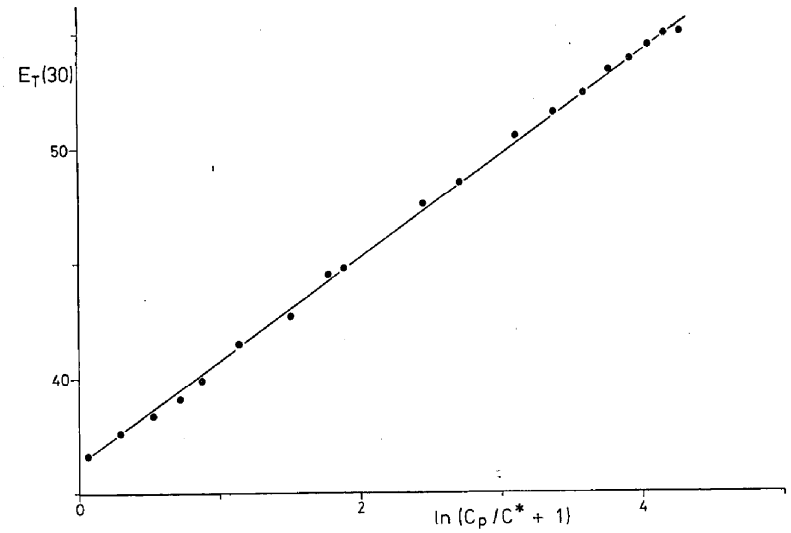


Figure 5. Relationship between $E_T(30)$ and ln (c_p/c^* + 1) for the methanol/dioxane mixture.

On the other hand, a plot of the $E_T(30)$ values versus ln c_p, where c_p is the molar concentration of the more polar component, results in a curve that has a linear section,[33] as is shown in Figure 4. At low concentrations of c_p, the polarity values of the straight line deviate and trend toward $c_p \rightarrow 0$ against the $E_T(30)$ value of the pure, nonpolar component. For the following discussion, the successful establishment of a two-parameter Equation (3) in closed form[33] describing the whole curve is crucial (see Figure 5).

$$P_G = E_D \cdot \ln (c_p/c^* + 1) + P_G^\circ \qquad (3)$$

P_G is the polarity of the mixture ($P_G = E_T(30)$ for dye **5**), and P_G° is the P_G value of the pure, less polar component (for example, the component with the smaller $E_T(30)$ value as a pure substance). c_p is the molar concentration of the more polar component. E_D (energy reach-through) and c^* (apparent concentration) are the parameters of the equation. Their meaning is specified by a limit analysis of Equation (3). The latter can be developed in a Taylor series for small c_p values in Equation (3). Breaking as usual after the second term results in Equation (4),

$$P_G = (E_D/c^*) \cdot c_p + P_G^\circ \qquad c_p << c^* \qquad (4)$$

where there is a linear relationship between P_G and c_p. At high values of c_p, $c_p/c^* + 1) \approx c_p/c^*$, and Equation (5) follows, which mathematically describes the observed linear section of the curve in Figure 4.

$$P_G = E_D \cdot \ln c_p + (P_G^\circ - E_D \cdot \ln c^*) \qquad c_p >> c^* \qquad (5)$$

By using Equations (4) and (5), the meaning of c^* becomes clear: For $c_p << c^*$, the contributions of the two components to the polarity are approximately additive. They act on the polarity scale in a first approximation independently of each other. For larger values of c_p, this is no longer valid. The mutual influence of both components appears according to Equation (3). E_D concretely represents the sensitivity with which the polarity scale responds to the addition of the more polar component, and c^* borders both of the mentioned areas. Equation (3) does not form a quantitative description of the polarities for dye **5**, depending on the composition of the binary mixtures, but covers all polarity scales investigated so far[33-37] (currently there are 10). In particular, their validity in the Winstein scale should be emphasized, as they are based on reaction kinetic measurements and not spectroscopic data, as mentioned above (see Figure 6). Thus, it can be assumed that Equation (3) describes a general polarity phenomenon and is not unique to solvatochromic systems. The number and diversity of the studied binary mixtures (at present, approximately 50[33-39]) gives rise to the fundamental validity of Equation (3) for binary systems.

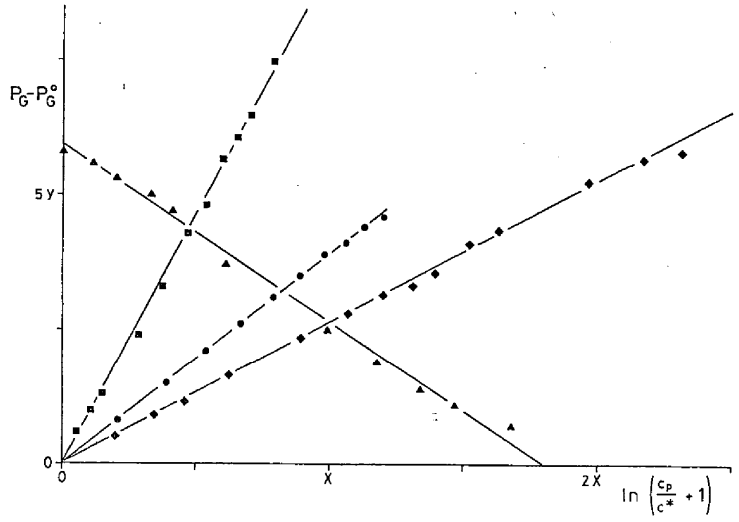


Figure 6. Linear relationship between P_G and ln (c_p/c^* + 1) for various polarity scales (Equation (3)).

- ◆ (diamonds) $E_T(30)$ methanol - acetone; $x = 2$, $y = 2$,
- • (circles) Y water - methanol; $x = 1$, $y = 1$
- ▪ (squares) Z methanol - acetone; $x = 2$, $y = 1$
- ▲ (triangles) π_1^* ethanol - *n*-heptane; $x = 1$, $y = 1$, ordinate: $P_G - P_G^\circ + 5.9$.

As a result, the quantitative relationship found is very widely applicable. For example, it is possible to determine the exact water concentration in organic solvents by means of a rapid test[38, 40] using Equation (3). The assembly of curved calibration graphs[31,41] is not required, which was previously a handicap in the use of solvatochromic systems for water determination.

Moreover, this method can be generalized to the determination of the composition of binary mixtures.[39,42]

Additionally, the reason why empirical polarity scales form a good linear correlation with each other for pure solvents, while commonly larger deviations occur[29] with mixtures, now has a satisfactory explanation based on Equation (3):[33,34]

A linear correlation in the polarity scales is to be expected if the contributions of both components to the total polarity are additive. This case is only realized over the entire concentration range if $c_p$max, the concentration of the pure polar component, is (substantially) smaller than c^* (see. Equation (5)). However, if c_p max is larger in relation to c^*, this relation becomes nonlinear, and deviations from a linear correlation in the polarity scales must be expected.

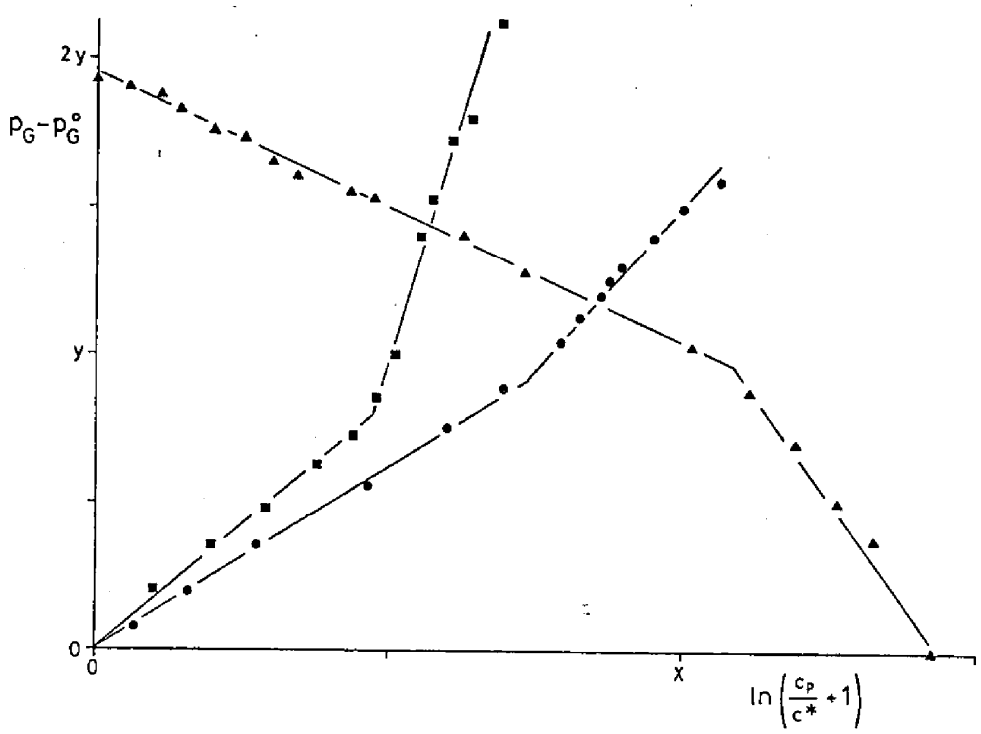


Figure 7. Double lines according to Equation (3) for a water/ethanol mixture.
• (circles) Y; $x = 2$, $y = 1$,
▪ (squares) $E_T(1)$; $x = 1$, $y = 4$,
▲ (triangles) π_l*; $x = 2$, $y = 4$; ordinate: $P_G - P_G^\circ + 7.7$.

Peculiarities in polarity behavior have been recognized in some cases by means of quantitative relationships between the polarity and the composition of mixtures (Equation (3)) and will be briefly described below. For some mixtures, e.g., ethanol with water (Figure 7), the formation of two different ranges in agreement with Equation (3) is observed[34] (double-line): For $c_p < c_k$ (c_k = critical concentration), normal behavior according to Equation (3) is observed. For $c_p > c_k$, however, the function changes into another analogue with different E_D and c^* values. The observed transition at c_k is very abrupt and provides a kink in the overall function (discontinuity in the first derivative). This situation, which occurs in various polarity scales, even in the Winstein scale, must be regarded as a property of the medium and could be due to a change in the solvent structure. For example, 1,4-dioxane is a "solvent structure breaker";[43] remarkably, the double line phenomenon is particularly pronounced in the dioxane-water mixture. Even more remarkable is the behavior of mixtures such as 1-butanol and nitromethane.[35] A plot of the polarity, e.g., as the $E_T(30)$ value, versus the concentration c_p of the more polar component (1-butanol) curves with a maximum at c_k, as shown in Figure 8. One must conclude that these mixtures are more polar than their components in certain concentration ranges. This result was unexpected, as it is contrary to the common opinion that the polarity of a mixture lies within the limits of the polarities of its components.

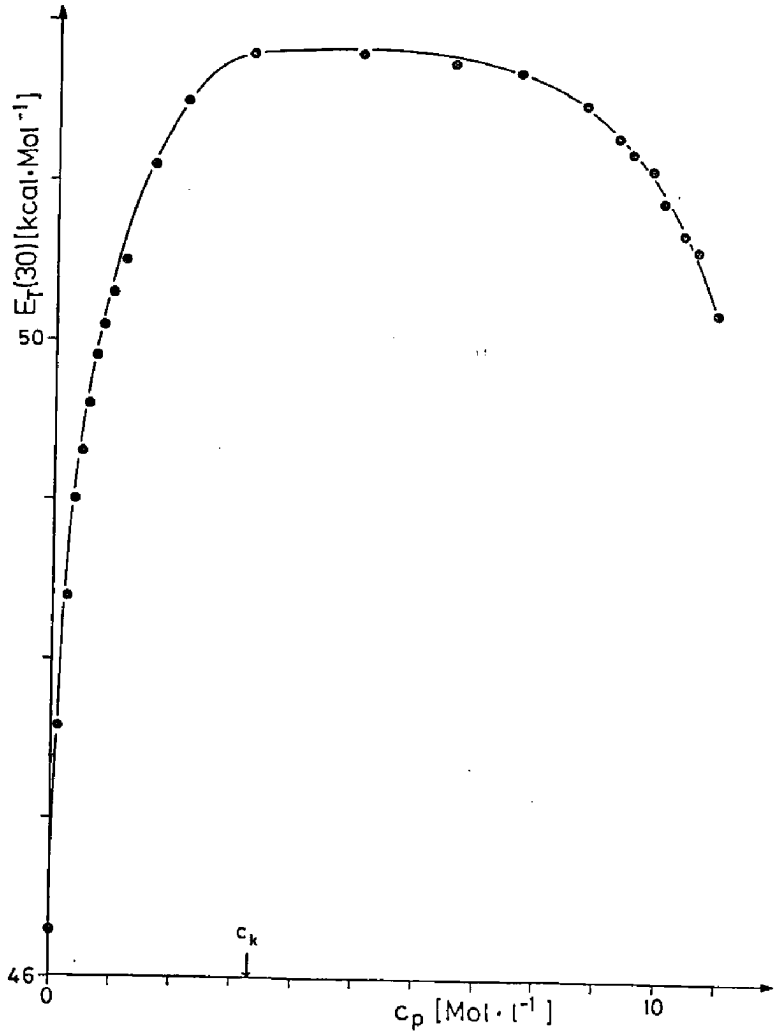


Figure 8. Polarity of a 1-butanol-nitromethane mixture as a function of the 1-butanol concentration (c_p).

Both branches of the curve in Figure 8 ($c_p < c_k$ and $c_p > c_k$) are verified by Equation (3), as shown in Figure 9. For $c_p < c_k$, normal behavior for a binary mixture is observed (Figure 9a). c_p is replaced by c_u, the molar concentration of the nonpolar component, in Equation (3) for the right branch of the curve in Figure 8 ($c_p > c_k$) (Figure 9b). The less polar component, nitromethane, thus acts in this concentration range as a more polar additive to 1-butanol. This increased polarity effect is defined as virtual polarity, P_V (for a more detailed treatment of this problem, see ref.[35]). This polarity boost phenomenon is not a special feature of the $E_T(30)$ scale. It is also observed in the χ_R scale[44], which is based on the strong positive solvatochromism of the absorbance of merocyanine **6** (RN 2913-22-6) (Figure 9c,d) and is thus probably a property of the binary mixture itself.[35] Typical systems with this peculiarity are combinations of C_2 to C_4 alcohols and dipolar aprotic solvents. The phenomenon is interpreted in terms of a hydrogen-bond donor-acceptor model. Interesting practical applications are expected.

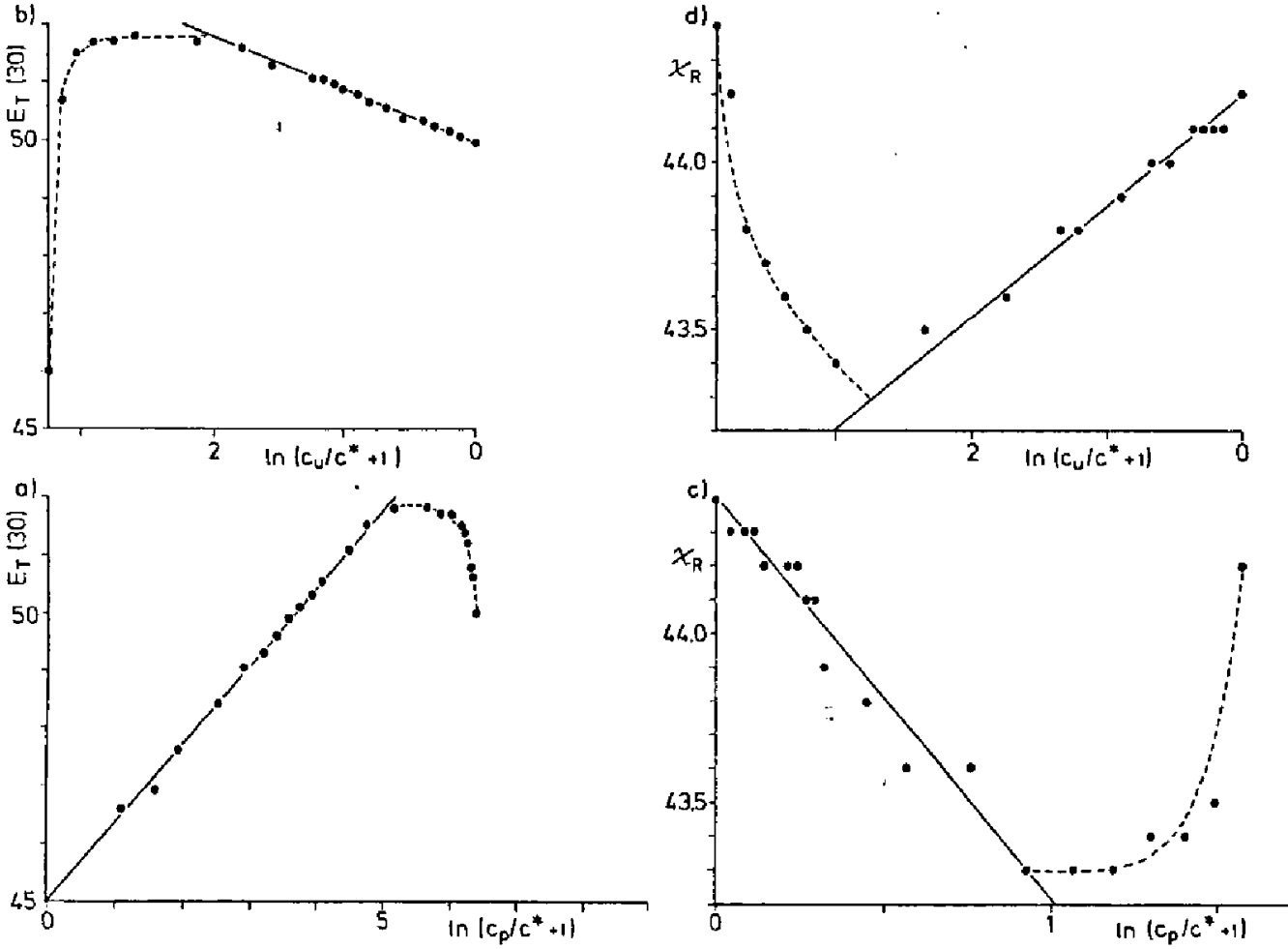
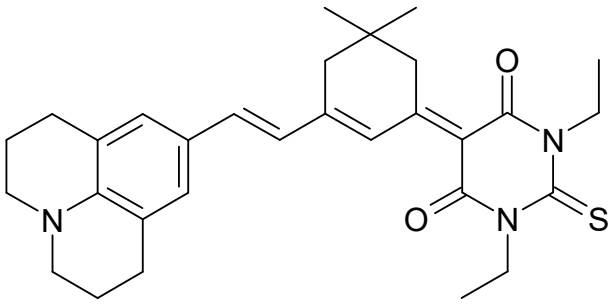


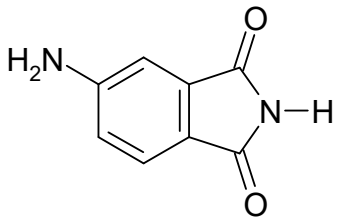
Figure 9. Relationship between P_G and ln (c_p/c^* + 1) and ln (c_u/c^* + 1) for a 1-butanol-nitromethane mixture.
(Left: P_G=E_T(30), right: P_G=χ_R.)



6

Finally, the causes of the deviations of the χ_R scale from the usual linear correlation of the polarity scales described in the literature[29,44,45] have to be clarified. As the previous section shows, this scale also satisfies Equation (3), including the specifics and should therefore generally reflect polarity effects. Their current special position can be described by an overall polarity scheme based on the polar behavior of dye **7** (RN 676-85-5), which exhibits a strong

solvatochromism in the fluorescence (Σ scale) and a weaker solvatochromism in the absorption (σ scale).



7

The laws of Franck-Condon transitions have to be taken into account[46] in the interpretation of solvatochromism during absorption and emission; thus, both the absorption and emission transitions take place as vertical processes much faster than occur in a nuclear motion. In addition, the initial and final states for the electron transitions must be distinguished:
In absorption, the initial state is the S_o ground state and the final state is the excited S_1 state; in fluorescence, it is the other way around: S_1 is the initial state and S_o is the final state. Due to the Franck-Condon principle, solvation by orientation of the solvent molecules can only occur at the initial states.[46,47] For the final states, on the other hand, only solvation via polarization effects is possible. The solvent-dependent behavior of an electron transfer becomes clear if S_o and S_1 differ appreciably in their polarity, as only the solvation effects due to polar solvents have to be taken into account in the more polar state. For example, in the $E_T(30)$ scale for dye **5**, the S_o state is polar, and the S_1 state is weakly polar. The absorption is therefore sensitive to the effects of solvent-orientation. In the following, this is called "polarity by orientation." The situation is different for the χ_R scale. For dye **6**, the S_o state is slightly polar, while the S_1 state is strongly polar.[45] The scale is therefore sensitive to displacement polarization but not to orientation; in the following, this phenomenon is called "displacement polarity" for short.
In earlier work[48,49] the refractive index has been used as a measure of polarizability. However, this is not free from a certain degree of arbitrariness, since it depends on the position of the sodium D-line and the position and shape of the absorption bands of the solvent in the UV range. The model described above is further supported by the influence of solvent on the spectral behavior of dye **7**. Due to its solubility properties, one can expect a low polarity S_o state, and because of the strong fluorescence solvatochromism, a strongly polar S_1 state. The absorption (σ scale) must therefore behave similarly to dye **6** and thus, the χ_R scale. In fact, we experimentally find a linear correlation between σ and the χ_R scale for various solvents. This can be seen in Figure 10.
On the other hand, opposite conditions are used for the fluorescence of **7** (Σ scale). The initial S_1 state is polar, the final S_o state is nonpolar. In the Σ scale, an orientation polarity should therefore be used, as in the $E_T(30)$ scale. Consistent with this concept, Figure 11 shows a linear relationship between the Σ and the $E_T(30)$ scale.
The χ_R scale thus is no longer unique among the polarity scales. It represents a typical measurement of the "displacement polarity," whereas the $E_T(30)$ scale includes mainly orientation effects with some partial effects of displacement polarizations, which can act cooperatively.

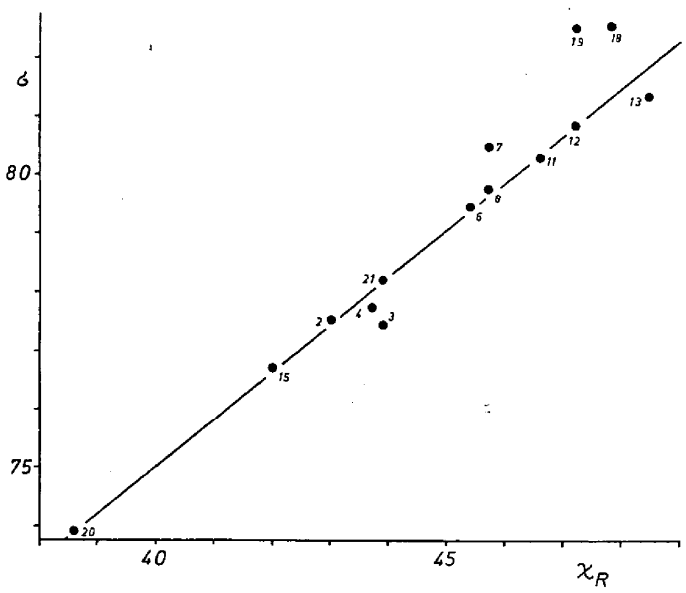


Figure 10. Linear relationship between σ and the χ_R scale. For solvents, see ref.[36)]

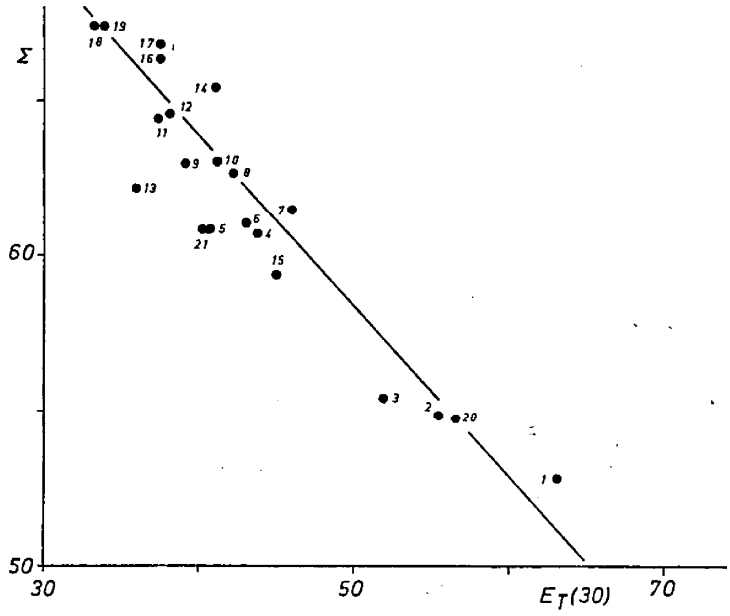


Figure 11. Linear relationship between Σ and the $E_T(30)$ scale. For solvents, see ref.[36)]

Extreme examples of this discrimination are found in solvent mixtures of water and methanol and in DMSO. Water and methanol behave as relatively polar substances based on orientation polarity measurements ($E_T(30)$ and Σ scale). DMSO is much less polar in comparison. However, when measuring the displacement polarity (χ_R and σ scale), the conditions are reversed: DMSO is much more polar than water. Remarkably, Equation (3) describes the polarity of binary mixtures with regard both to the orientation of the molecules as well as their polarizability.

The relationships mentioned above clarify why a plot of the wavenumbers of the absorption and emission spectra of a substance in various media generally will not result in a linear relationship.[47)] Depending on the polarities of the ground state and the excited state, the

orientation polarity and the displacement polarity dominate for most dyes; however, the polarity differences between the ground and excited states are not as distinct as they are in the $E_T(30)$, χ_R and Σ scales.

The present theoretical basis allows for the design of a system in PMMA (*Plexiglas*) in which the absorption and the emission are spectrally well-separated. Since the polarity of PMMA is relatively low ($\Sigma = 62.6$, and from this $E_T(30) = 42.2$ can be calculated) - it is comparable to the polarity of acetone - suitable dyes (among other things for solubility reasons) should have low polarity S_o states. The S_1 (or S_1') state should be polar according to the modification mechanism (Figure 3). A good model is therefore dye **7**. In Figure 12, the already good spectral separation ($Tz = 36$) in pure PMMA is shown. For large-scale collectors, an even better separation is desirable for the reasons mentioned above, which could be realized by making additions to PMMA. One can conclude from the approaches mentioned above that DMSO, for example, is not suitable as an additive since it shifts the absorption to longer wavelengths in relation to the emission. This shift causes a net loss (or only a slight improvement) in the spectral separation. Therefore, in a model experiment, methanol was used as an additive, and the emission was shifted to become more bathochromic in relation to the absorption. This result is shown in Figure 13 with a separation number of 98; a system has thus been obtained with a spectral separation that is sufficient for practical use.

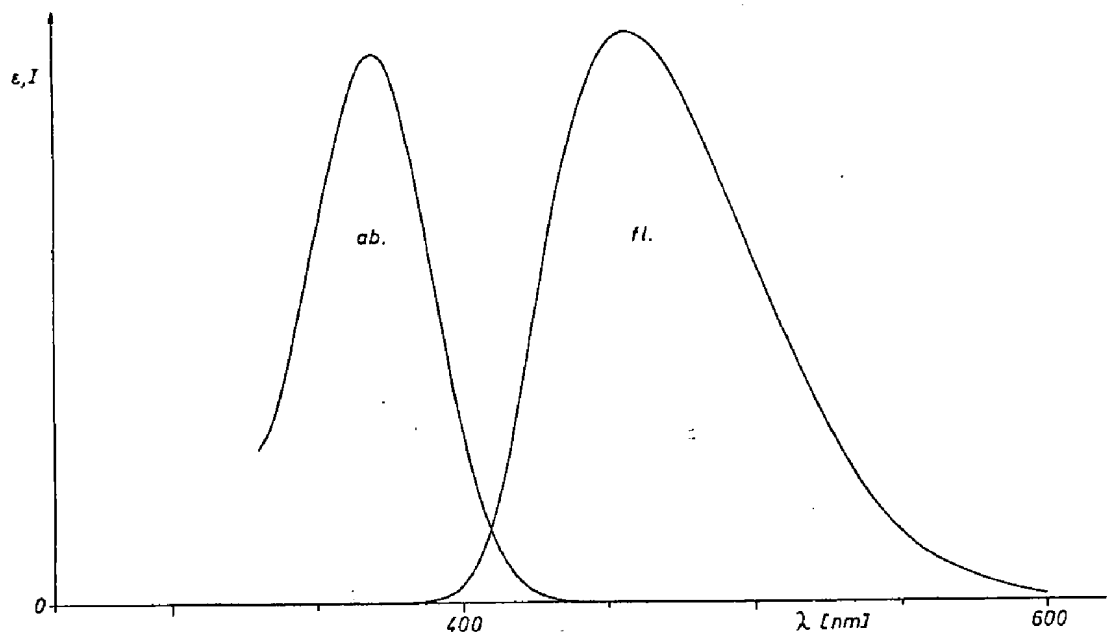


Figure 12. UV/VIS absorption and fluorescence spectra of **7** in PMMA (*Plexiglas*).

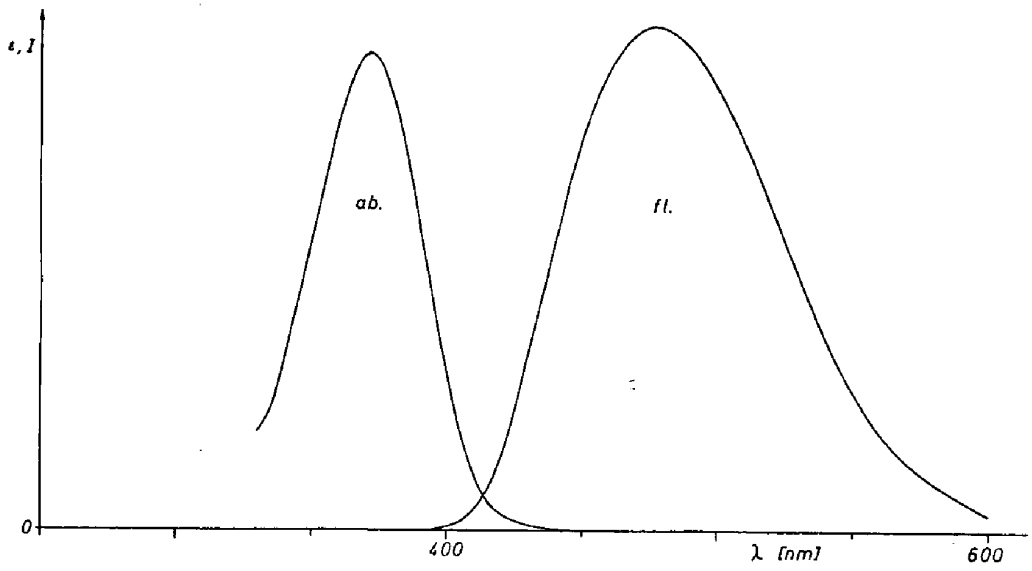


Figure 13. UV/VIS absorption and fluorescence spectra of **7** in PMMA with the addition of 10% methanol.

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